

EIS evaluation of the filiform corrosion of aluminium coated by a cataphoretic paint

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Abstract

Filiform corrosion is mainly considered as a cosmetic attack and is undesirable in most applications. The initiation and propagation of the filaments are related to different parameters such as the presence of defects, the permeability of the coating to water and oxygen, the adherence of the paint system and the presence of salts.

The aim of this work is to study the behaviour of painted aluminium samples towards filiform corrosion or delamination. The 6082 Aluminium alloy was selected and the samples were covered with a cataphoretic epoxy primer without lead (PPG Industries France). Prior to the application of the electrocoat, the samples were pre-treated by a commercial Zr/Ti or chromate conversion treatment or simply etched with a commercial acid etching product.

Filiform corrosion was studied by the normalized test (ISO/DIS 4623): painted and scratched samples were inoculated in HCl and exposed in a constant humidity chamber at 40 °C and 82% RH for 3 weeks. After exposure the samples were subjected to a visual and optical microscopic examination.

Electrochemical impedance spectroscopy was used to study the sensitivity to filiform corrosion. The operating mode of this test is similar to the normalized one. The samples were scratched before inoculation for 1 h in HCl and then exposed to the humidity chamber for a maximum of 4 days. The samples were tested by EIS in an acidified 0.1 M Na₂SO₄ electrolyte solution. The resulting impedance spectra were analyzed with an appropriate equivalent electrical circuit which allows the evaluation of the exposed metallic surface area, directly related to the extent of filiform corrosion or delamination. Different parameters were varied: the exposure time in the humidity chamber; the immersion time in the electrolyte sulphate solution as well as its pH and the coating thickness.

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1. Introduction

Aluminium alloys are known to be particularly sensitive to filiform corrosion. This corrosion type is mainly a cosmetic attack because in most cases it does not weaken or destroy the metallic structure and concerns only the surface appearance. Filiform corrosion is a specific delamination which occurs only under atmospheric conditions with relative humidity between approximately 50 and 90%. Small threadlike delamination tracks are formed which in general follow irregularities on the surface (either rolling or grinding marks). This specific

type of delamination is driven by a differential aeration cell. In most cases, it is related to anodic undermining [1]. Galvanic corrosion is created between the head front of the filament (anode) and the tail (cathode). This corrosion is controlled by many parameters: the metal substrate, the surface preparation, the presence of defects, the permeability of the coating to water and oxygen, the adherence of the paint system and the presence of salts. As shown in different publications [2–4], the substrate preparation prior to coating (chemical etching, mechanical abrasion, or application of a pre-treatment) considerably affects the sensitivity to filiform corrosion.

Numerous papers refer to the efficiency of electrochemical impedance spectroscopy (EIS) as a tool for the evaluation of adherence properties of organic coatings [5–9]. Moreover, a

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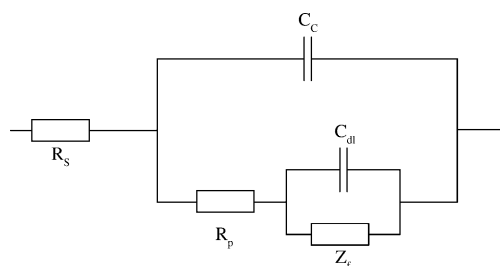


Fig. 1. Equivalent electrical circuit where R_s is the bulk electrolyte resistance, C_c the coating capacitance, R_p the pore resistance of the coating, C_{dl} the double layer capacitance and Z_f an element representing the faradic impedance.

recent work published by Fedrizzi et al. [10,11] shows that the sensitivity to filiform corrosion can also be revealed by EIS. This method is based on the electrical equivalent model proposed by Kendig. This circuit, shown in Fig. 1, consists of two time constants. The first time constant, observed at high frequency, is related to the coating properties. In the case of a very low coating capacitance (10^{-10} F/cm²) and a large defect for the scratched samples, this time constant is generally shifted towards higher frequencies than those reached with usual procedures.

The second time constant, at low frequency, takes into account the corrosion reaction of the substrate. This time constant is characterized by the double layer capacitance C_{dl} and the element Z_f which contains the charge transfer resistance R_{ct} and electrical elements taking into account the low frequency behaviour which appears when complex aluminium dissolution reactions take place [12]. C_{dl} and R_{ct} are two parameters used to specify the delamination or filiform corrosion of the coating. The wet or active metal area is proportional to the electrical parameters related to the time constant. From the C_{dl} values, it is possible to obtain information on the wet area (A_w) following the equation:

$$\frac{C_{dl}}{C_{dlo}} = A_w$$

where C_{dlo} is the double layer capacitance of the bare metal. All the capacitances are mathematically modelled using a constant phase element (CPE) in order to consider non-ideal behaviour.

Such an equivalent circuit is valid for the study of scratched organic coatings given that the resistance under the film is sufficiently low. The authors selected an acidified electrolyte solution (0.1 M Na₂SO₄ at pH = 2) able to dissolve the corrosion products formed under the coating during the exposure to the humidity chamber. The immersion time in the electrolyte solution seems to be an important parameter. Actually, the immersion has to be long enough to dissolve the corrosion products formed in the humidity chamber. However, too high immersion times may be accompanied by the growth of new corrosion products due to the reaction of the metal with the testing electrolyte [4].

Beyond the opportunity to get quantitative information about filiform corrosion, this technique also allows a rapid acquisition of data compared to the classical evaluation of this type of corrosion. Starting from this measurement procedure, we studied whether it is possible to use EIS to predict the filiform corrosion behaviour of electro-coated aluminium samples in a short time. We tried to define the best operating parameters for carrying out this test and to answer the following question: is this test able to distinguish delamination from filiform corrosion and define the susceptibility to filiform corrosion of a substrate/pre-treatment/coating system.

In order to improve corrosion resistance and coating adhesion, the aluminium alloy plates are generally subjected to a conversion treatment. Until now chromates were widely used as anticorrosive pre-treatment for aluminium alloys. However, hexavalent chromium presents very high toxicity and has a bad environmental impact. New types of pre-treatment of aluminium surfaces are currently proposed. Beyond their inhibitive efficiency against corrosion, their efficiency towards paint adherence and protection against filiform corrosion is tested. Among the different alternatives to chromates, zirconium-based conversion pre-treatments show good results in adherence improvement with different organic coatings and good anti-corrosion properties [13,14]. Accordingly, we compared chromate pre-treated aluminium to samples treated with a commercial Zr/Ti conversion bath. The applied coating is a recently generated epoxy cataphoretic primer used in the car industry [15,16].

2. Experimental

2.1. Materials

Filiform corrosion and electrochemical impedance spectroscopy tests were carried out on the 6082 aluminium alloy. The composition of this alloy is summarized in Table 1. The test panels (100 mm × 50 mm × 1 mm) were pre-treated by degreasing with acetone followed by a 10 min etching in a commercial acid bath (Henkel Ridoline[®] 124 N + Novox Activator[®] 12B) at 25 °C. The samples were then subjected to a chemical conversion treatment using commercial products in order to obtain a chromate or a Zr/Ti coating. Some samples were coated after etching without being pre-treated.

Table 1
Chemical composition (wt.%) of the AA 6082 aluminium alloy

Al	97.10
Si	0.92
Mg	0.745
Fe	0.344
Mn	0.821
Cu	0.030
Cr	0.0036
Ti	0.0243
Zn	0.0113

A commercial anticorrosive and toxic pigment free (without lead) cathaphoretic epoxy coating (PPG Industries, France) of a new generation was electrodeposited on the aluminium plates using a constant voltage method. The applied voltage was 300 V and the bath temperature was 30 °C. After coating for 3 min, rinsing and curing at 180 °C for 30 min, the film thickness measured by a Minitest 3001 thickness gauge was $30 \pm 0.9 \mu\text{m}$.

2.2. Filiform corrosion standard test

For the classical filiform corrosion test the panels were subjected to the ISO/DIS 4623 standard. A scratch of 43 mm in length and 1 mm in width was produced in longitudinal and traverse directions. Filiform corrosion was inoculated by exposure to HCl vapours for 1 h and the samples were then placed in a humidity chamber with $82 \pm 3\%$ relative humidity and 40 ± 2 °C. Visual observation was carried out after 7, 13 and 21 days of exposure and the extent of filiform corrosion was quantitatively assessed by measuring the lengths and the number of filaments using a LEICA MZ12 image analyser.

2.3. Electrochemical measurements

EIS measurements were carried out on scratched coated samples following the procedure proposed by Fedrizzi et al. [4] The coated samples used for this test were scratched with a cutter reaching the metallic substrate. The linear defect produced was 2 ± 0.02 cm long and $40 \mu\text{m}$ width with an area of about $0.8 \text{ mm} \times 0.8 \text{ mm}$. The scratches were performed in orthogonal direction with respect to the rolling marks. The width and area of the defect were controlled with the help of an optical microscope (Nikon).

The procedure used to initiate and propagate filiform corrosion was the same as adopted in the ISO/DIS 4623 standard but with a shorter exposure time (maximum 96 h) in the humidity chamber. The samples were then analyzed by EIS at room temperature in 0.1 M Na_2SO_4 acidified at pH ranging from 1 to 3 by adding sulphuric acid. Different immersion times in the electrolyte solution were explored. Each measurement was repeated three times, each time using a different sample.

A conventional three-electrode cell was used for the electrochemical tests. The working electrode was the investigated sample; the exposed area was 4.9 cm^2 . The counter electrode was a platinum plate and all potentials were measured with respect to an Ag/AgCl reference electrode.

The impedance measurements were carried out over frequencies ranging from 100 kHz to 10 mHz using a 5 mV amplitude signal voltage in a Faraday cage in order to minimize external interference on the system. The impedance spectra were acquired using a frequency response detector EG&G 1025 coupled with an EG&G 283 potentiostat. Both devices were computer controlled using Powersuite® software. The impedance data were analyzed by using ZsimpWin® software.

3. Results

3.1. Standard test

The ISO/DIS 4623 normalized test was performed for three weeks. The samples underwent a visual and optical microscopic examination after exposure times of 7, 13 and 21 days, respectively.

The etched samples coated without any pre-treatment showed a visible degradation after 7 days of exposure (Fig. 2a). Actually, many blisters were already detected representative of a delamination phenomenon instead of filiform corrosion. For the chromated samples, the coating was intact without any visible defect. On the Zr/Ti treated samples, visual and optical examinations revealed 4 filaments per centimetre with a length of half millimetre.

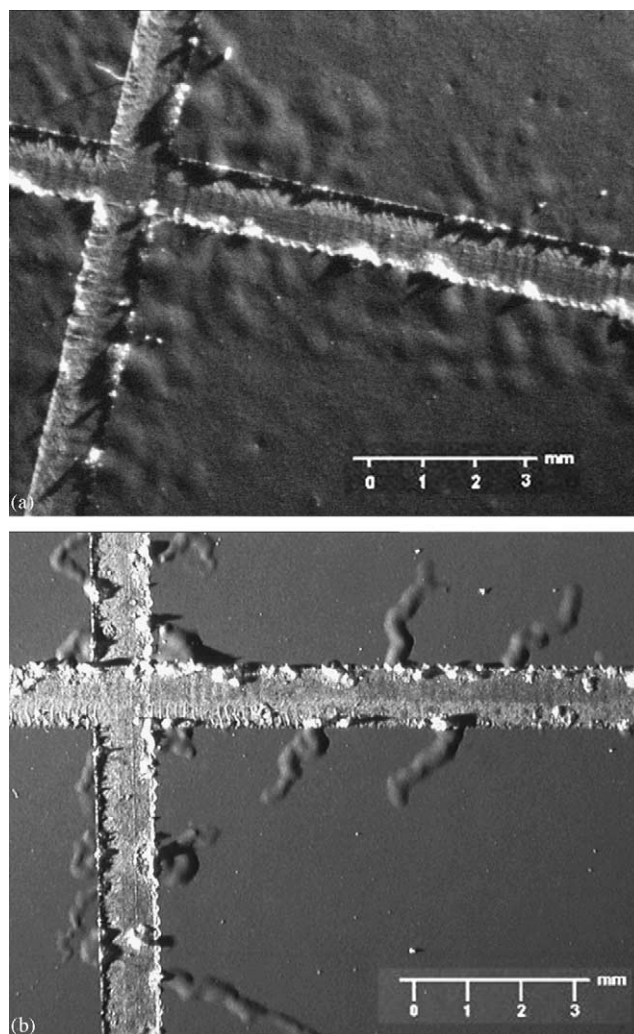


Fig. 2. Optical microscope photographs of electrocoated aluminium 6082 samples which were subjected to a normalized filiform corrosion test: after 7 days of exposure to the humidity chamber for a simply etched sample (a), and after 21 days of exposure for a sample pre-treated with a Zr/Ti conversion coating (b).

Table 2
Results of the filiform corrosion test (ISO/DIS 4623 standard)

Pre-treatment	After 7 days	After 13 days	After 21 days
None	Disbonding over 2 mm	Disbonding over 3 mm	Disbonding over 5 mm
Chromatation	No degradation	2 filaments/cm Length: <1 mm	2 filaments/cm Length: ≤1 mm
Zr/Ti	4 filaments/cm Length: 0.5 mm	4 filaments/cm Length: 1 mm	4 filaments/cm Length: 1–3 mm

After 13 days, filiform corrosion also started on the chromated samples with an average value of 2 filaments per centimetre with a length inferior to half millimetre. For the Zr/Ti specimens, the filament length increased up to 1 mm. After 21 days of exposure, the delaminated area on the etched samples reached more than one centimetre on both sides. The growth of filaments continued for the pre-treated samples, filiform corrosion being more developed on the Zr/Ti specimens (Fig. 2b). The results obtained up to 21 days are summarized in Table 2.

To recapitulate, for the 6082 aluminium alloy, the application of a conversion pre-treatment before painting has an important effect on the filiform corrosion resistance, the best performance being obtained with the chromate conversion treatment.

The exposure time of the samples to HCl vapours was varied in order to optimize the initiation of filaments and to observe their growth within short times of exposure to humidity. For this purpose, a classical filiform corrosion test was carried out after 10, 20, 30, 60 and 120 min of exposure to HCl vapours on the differently treated samples. Fig. 3a and b show the delamination width (for a sample coated without pre-treatment) or the number of filaments (for a chromated sample) as a function of the exposure time in the humidity chamber. The exposure time to HCl seems not to affect the delaminated area for samples coated without pre-treatment. However, in the case of chromated samples, it is clear that inoculation shorter than one hour with HCl does not allow the observation of filament growth for an exposure time in the humidity chamber inferior to 4 or 5 days. On the other hand, for exposures to HCl longer than 1 h, the increase of damage is not significant. Consequently the exposure time to HCl vapours was maintained at 1 h as in the normalized test.

3.2. EIS detection of filiform corrosion

3.2.1. Influence of the pre-treatment

Impedance data in the Bode phase representation obtained for each different pre-treatment are given in Fig. 4 after 1 h immersion in a sodium sulphate solution at pH 2 and for different exposure times in the humidity chamber. The impedance modulus is fairly sensitive to the increase of the exposure time. As it is the most sensitive to the evolution of filiform corrosion (the different time constants can be clearly distinguished), only the Bode-phase dia-

grams are used to discuss the different results presented in this paper.

For exposures shorter than 24 h, only one time constant is observed, whatever the preparation of the samples before coating. After longer exposures, the Bode diagram progressively shows the presence of two time constants. For samples coated after etching without any pre-treatment, these two time constants were detected after 24 h of exposure, while on pre-treated samples an exposure time in the humidity chamber of 48 h is necessary to clearly distinguish the two time constants. Moreover, for the same exposure time in the climatic cham-

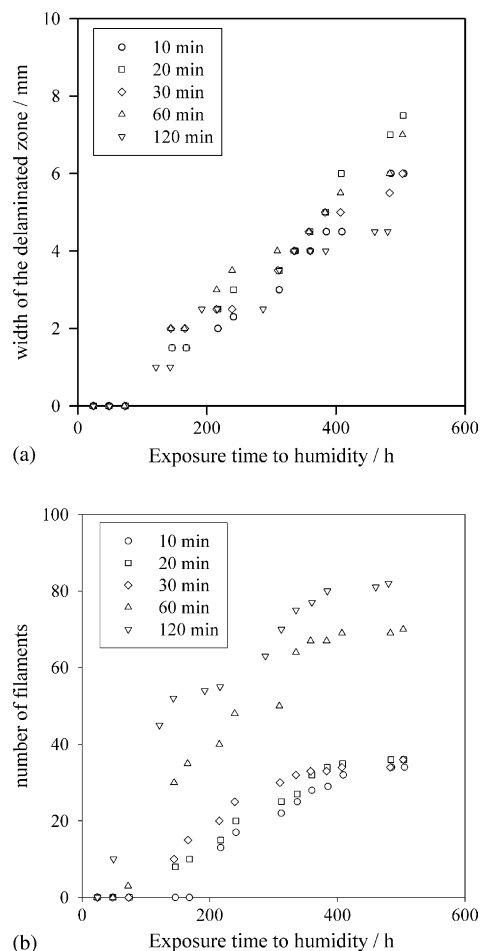


Fig. 3. Growth of filaments or blisters as a function of the exposure time to HCl vapours for aluminium samples electrocoated after etching without pre-treatment (a), or after a chromatation conversion treatment (b).

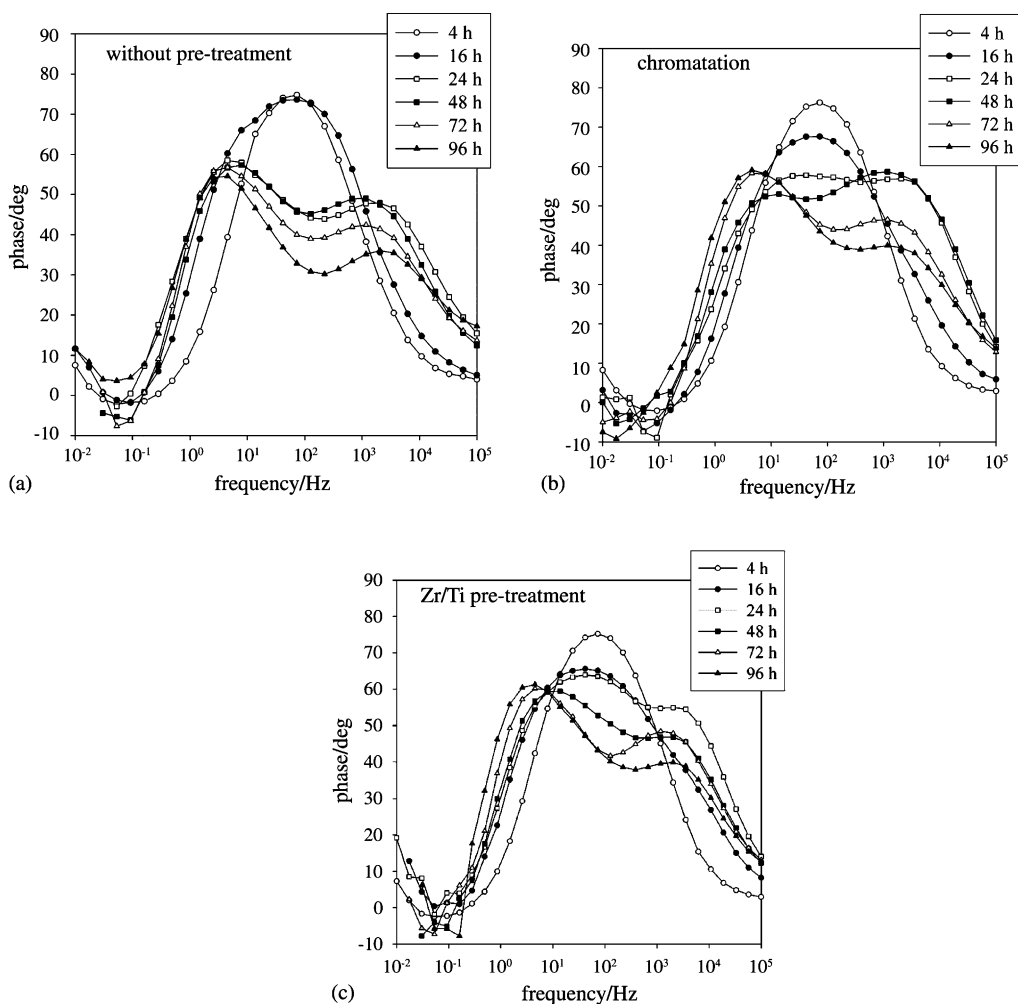


Fig. 4. EIS data in the Bode phase representation for different exposure times to humidity of scratched samples: (a) without pre-treatment; (b) chromated samples; (c) aluminium treated with Zr/Ti. Measurements carried out after one hour of immersion time in the sulphate electrolyte solution at pH 2.

ber, the two constants are more easily discernible for the Zr/Ti conversion than for the chromation pre-treatment. This suggests the existence of a correlation between the sensitivity to delamination or filiform corrosion and the appearance of a second time constant in the Bode phase diagrams. Actually, for electrochemical measurements carried out at pH 2, we observed that the more the samples are sensitive to filiform corrosion, the more quickly the two time constants are observed.

The single time constant, observed for short exposures, may be assigned to the corrosion reaction of the exposed metal. At this time, no degradation at the metal/coating interface due to filiform corrosion or delamination has yet occurred. When the exposure time increases, the second time constant which appears is probably related to the corrosion products present under the coating, inside the filaments or blisters.

3.2.2. Influence of the coating thickness

To confirm that the time constant in the high frequency range is not due to the coating properties, the film thickness

was varied by changing the temperature of the cathodic coating bath. Actually, an increase of the film thickness increases its barrier properties and reduces the coating capacitance C_c which causes a shift of the coating time constant towards higher frequencies.

The Bode phase curves obtained for different film thicknesses are shown in Fig. 5. For the same pre-treatment, the two time constants observed by EIS appear at the same frequency and show the same magnitude whatever the film thickness. Consequently, these results seem to confirm that the time constant observed at high frequencies is effectively due to the corrosion products under the coating and not to the coating properties. It is also possible to reach this conclusion from the capacitance values which are some orders of magnitude higher than those measured on intact coatings ($\sim 10^{-9}$ F). The capacitance can especially be estimated from the impedance modulus versus frequency curves. As shown in Fig. 5 for a coating without pre-treatment, the capacitance of the high frequency time constant is of the order of 10^{-5} F independent of the coating thickness.

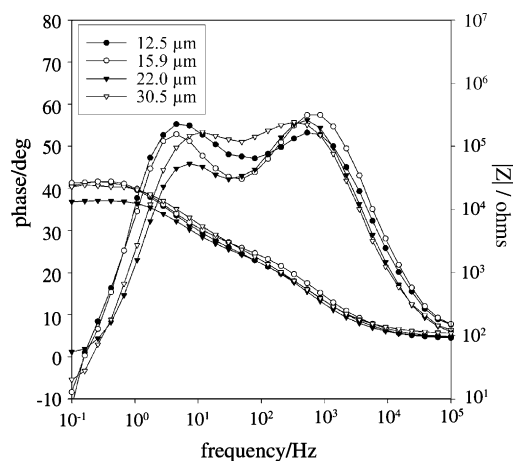


Fig. 5. Bode-phase diagrams for different cathoretic coating thicknesses of scratched samples without pre-treatment. Data obtained after 48 hours of exposure to humidity chamber and 4 h of immersion in a sulphate electrolyte solution at pH 2.

3.2.3. Effect of immersion time

As observed, immersion for 1 h in a sodium sulphate solution at pH 2 does not allow the dissolution of the corrosion products formed under the coating. Moreover, the low-frequency time constant is displaced to lower frequencies indicating a slow down of the process which can be explained by the contribution of a diffusion process in the electrochemical process occurring at the metal/electrolyte interface [17]. Such impedance data cannot easily be analysed with the usual equivalent circuit such as that proposed by Kendig. Some alternative models were proposed by Fedrizzi et al. [11] taking into account the presence of aluminium corrosion products under the coating. Though closer to our observations, this model is not adequate to describe the impedance spectra given that in the present case the two time constants partially overlap.

As a consequence, while there is a good correlation between the electrochemical measurements and the normalized test, the information obtained by EIS for one hour of immersion in the electrolyte solution at pH 2 is only qualitative.

To have a better assessment of the extent of filiform corrosion, the experimental parameters should be adapted to increase the dissolution of the corrosion products formed under the coating. Longer immersion times in the electrolyte solution were then explored. An immersion of 4 h allows the dissolution of the corrosion products locally present in the defect. This immersion time is however not long enough to avoid the appearance of the second time constant in the Bode plots. The dissolution of corrosion products formed inside the filaments or blisters during the exposure in the humidity chamber needs in our case immersion times of minimum 8 h in the electrolyte solution at pH 2 (Fig. 6).

3.2.4. Effect of pH

In order to enhance the dissolution of the corrosion products in a shorter time, measurements were also carried out

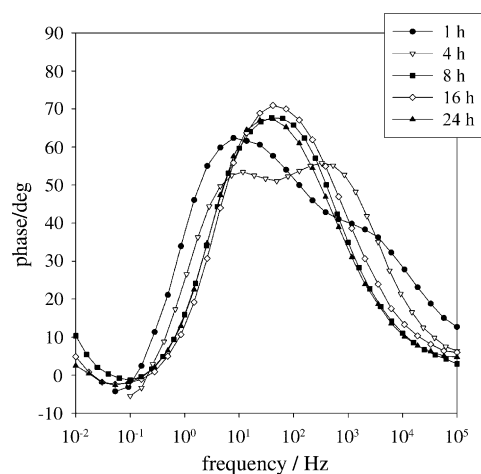


Fig. 6. Bode-phase diagrams for different immersion times in the sulphate electrolyte solution at pH 2. Data obtained with aluminium samples etched and electrocoated without any pre-treatment; exposure time in the humidity chamber: 48 h.

at pH 1. The impedance data in the Bode phase representation obtained after 48 h in the climatic chamber, 4 h in the test solution at pH 1 are shown in Fig. 7. To get a better understanding of the influence of pH, measurements were also made at pH 3.

By acidifying the electrolyte solution, the corrosion products are dissolved within shorter immersion times and thus, the time constant due to corrosion products in the impedance data disappears. On the contrary, after 4 h of immersion in the electrolyte solution at pH 3, the time constant related to the corrosion products is more pronounced than at pH 2. Moreover, the important shift through lower frequencies of the time constant associated with the electrochemical reaction can be explained by a higher contribution of a diffusion process than at pH 2. At pH 1, the observed time constant is only related to

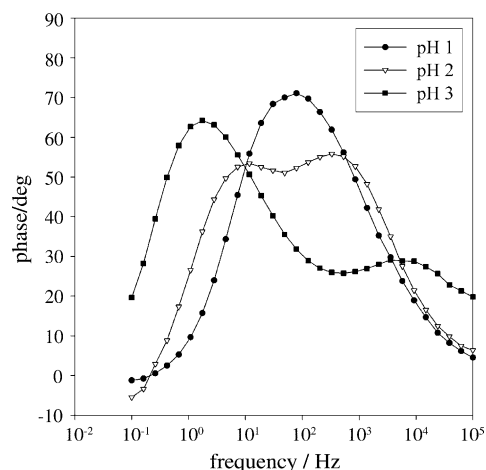


Fig. 7. Bode-phase diagrams at different pH of the sulphate electrolyte solution. Aluminium samples coated without pre-treatment; data obtained after 48 h of exposure to humidity chamber and 4 h of immersion in the electrolyte solution.

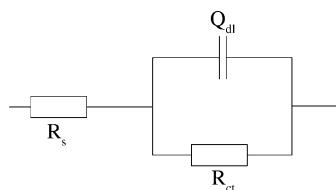


Fig. 8. Electrical equivalent circuit where R_s is the bulk electrolyte resistance, R_{ct} the charge transfer resistance at the metal/electrolyte interface and Q_{dl} the non-ideal double layer capacitance (CPE).

the electrochemical reaction at the metal/electrolyte interface in the scratch and inside the filaments.

3.2.5. Determination of the exposed metal area

The achievement of a single time constant allows Q_{dl} to be obtained by fitting the experimental curves with the simplified electrical equivalent model (Fig. 8). The Q_{dl} values are shown in Fig. 9 as a function of the exposure time to the humidity chamber. Values of the active metal area A_w can be obtained by dividing the Q_{dl} values by the double layer capacitance of the bare metal (assuming that Q_{dl0} is constant). As observed by Fedrizzi et al. [4], the determination of the double layer capacitance of the bare metal is a critical step as measurements on uncoated pre-treated samples can lead to an erroneous estimation of Q_{dl0} . Indeed, the exposed metal after the scratch may differ markedly from an uncoated pre-treated surface. In this work the experimental value of Q_{dl0} was determined with non-exposed scratched samples immersed in Na_2SO_4 0.1 M at pH 1. After dividing by the scratch area (0.8 mm^2), the obtained values of Q_{dl0} varied between 1.1×10^{-6} and 1.3×10^{-6} F. Q_{dl0} depends little upon the pre-treatment in agreement with a deep scratch reaching the metal under the pre-treatment layer. Moreover, at this time no adhesion loss or corrosion have occurred so far so that the role of the pre-treatment is probably negligible.

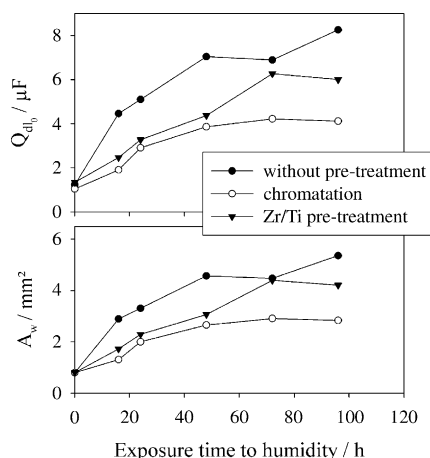


Fig. 9. Q_{dl} values and calculated active metal area (A_w) as a function of the exposure time to the humidity chamber for different pre-treatments. Experimental conditions: 4 h of immersion in a sulphate electrolyte solution at pH 1.

The calculated values of the exposed metal area A_w are shown in Fig. 9. For all the pre-treatments, an increase of A_w is observed as a function of the exposure time to humidity, in agreement with the progressive growth of filaments or blisters. The highest values of exposed metal area are observed for samples coated without application of any pre-treatment. When a conversion treatment is applied on the samples before the cathaphoretic coating the values of A_w are smaller reflecting the decrease of sensitivity to delamination, the lowest values being obtained with chromatation.

Consequently, the quantitative data obtained with impedance measurement carried out at pH 1 follow the same sequence as those qualitatively observed at pH 2 (for short immersion times in the electrolyte), which agrees with observations made with the normalized filiform corrosion test.

The best sensitivity of this method is obtained for the shortest exposure time in the climatic chamber. The slope of the curve A_w as a function of exposure time in the climatic chamber obtained for $t \rightarrow 0$ can be used as a parameter to distinguish delamination from filiform corrosion. Actually, for exposure times inferior to 24 h, the slope for the etched sample is double that obtained for the pre-treated ones.

4. Conclusions

The sensitivity to filiform corrosion of a substrate (6082 aluminium alloy)/pre-treatment/cathaphoretic electrocoating was studied by two methods: the ISO/DIS 4623 standard and electrochemical impedance spectroscopy. After initiation of filiform corrosion by HCl vapours, the scratched samples were exposed to a climatic chamber (40°C , 82% RH) for short times (maximum 96 h).

It is possible to define by EIS the susceptibility to filiform corrosion of a substrate pre-treatment coating system. Indeed, EIS measurements obtained for short immersion times in a sodium sulphate solution at pH 2 show the presence of two time constants for exposure times in the climatic chamber longer than 48 h. The low frequency time constant was assigned to processes occurring at the electrolyte/metal interface while the high frequency time constant was attributed to the corrosion products under the coating. A qualitative analysis of these data allowed us to observe a direct correlation between the appearance of the high frequency time constant and the sensitivity to filiform corrosion.

Furthermore, to obtain quantitative values for the wet or the active area, EIS measurements were carried out after a long immersion time in the electrolyte solution or lower pH. These conditions are indeed necessary to dissolve the corrosion products under the coating accumulated during exposure to humidity and to obtain values of the active metal area (A_w) with the help of a simplified equivalent electrical circuit. The EIS results showed a good correlation with the visual observations made with the standard filiform corrosion test. The main advantage of the EIS method is the opportunity to obtain a quantitative evaluation (A_w) of the sensitivity to filiform

corrosion within a very short time (after 24 h instead of 21 days).

Finally, the trend of the values of A_w at short exposure times to humidity could be used to differentiate delamination from filiform corrosion as the increase is double for the samples coated without any pre-treatment. The best sensitivity is also obtained for the short exposure time in the climatic chamber (inferior than 24 h).

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